Supplementary Information Material

Tautomers and electronic states of jet-cooled 2-aminopurine investigated by double resonance spectroscopy and theory

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(submitted to PCCP 2005)

Additional information about the nature of the electronically excited state can be obtained by comparing the vibronic frequencies and intensities of 2AP as obtained from the R2PI measurements data with theoretically determined harmonic vibrational frequencies and FC factors. In doing so, great care must be exercised. Particularly in the low-frequency vibrations, the atoms are expected to carry out large amplitude motions where anharmonicity effects - not included in the theoretical treatment - are important. Uncertainties arise also from experimental intensity data. For recording the experimental spectrum over a broad wavelength region, several dyes are utilized and one has to make sure that intensities are comparable in overlapping regions. Furthermore, the laser power has to be tuned low to prevent saturation artifacts. Finally, comparing FC factors with experimental intensity variations implicitly makes use of the assumption that the electronic transition dipole moment is insensitive to changes in the nuclear coordinates which might not be the case. Keeping all these reservations in mind we note that the measured intensities in the R2PI spectrum (Fig. 1) bear a larger resemblance to the quantum chemically determined FC-factors (c.f. Fig. S1) of 9H-2AP than to those of 7H-2AP. Particularly in the low frequency regime, we find larger displacements for the vibrational coordinates of 9H-2AP in the electronic ground and first excited $^1\pi\pi^*$ states. As a consequence, the computed $^1\pi\pi^*$ vibronic spectrum of 9H-2AP is much denser than its 7H-2AP counterpart. In the energy range between the origin and 2000 cm^{-1} above we find roughly 33000 lines in the 9H-2AP spectrum, compared to about 19000 for 7H-2AP. In both cases, the 0-0 transition exhibits the largest FC factor. The intensity pattern of the first four experimental peaks located at 169, 220, 272, and 329 cm^{-1} above the origin (strong/medium/medium/strong) is nicely matched by those of the computed lines at 146, 242, 271, and 322 cm^{-1}. The lines at 146 and 271 cm^{-1} originate from the excitation of one vibrational quantum of the corresponding out-of-plane motion of the molecular frame whereas the line at 322 cm^{-1} is due to the lowest in-plane vibrational transition. Interestingly, the line at 242 cm^{-1} is a combination band of the 146 cm^{-1} mode and one quantum of the lowest frequency vibrational mode of $^1\pi\pi^*$ excited 9H-2AP. The fundamental transition of the latter mode at 96 cm^{-1} has low intensity as seen in Fig. S1. A detailed comparison of higher-lying transitions is difficult as the experimental spectra become broader and the errors in the computed vibrational frequencies accumulate. In 7H-2AP, the first vibronic transition with substantial intensity is predicted to lie 324 cm^{-1} above the origin, i.e., considerably higher than the experimentally observed bands. These findings further support the assumption that only 9H-2AP is present in the molecular beam to an appreciable extent.

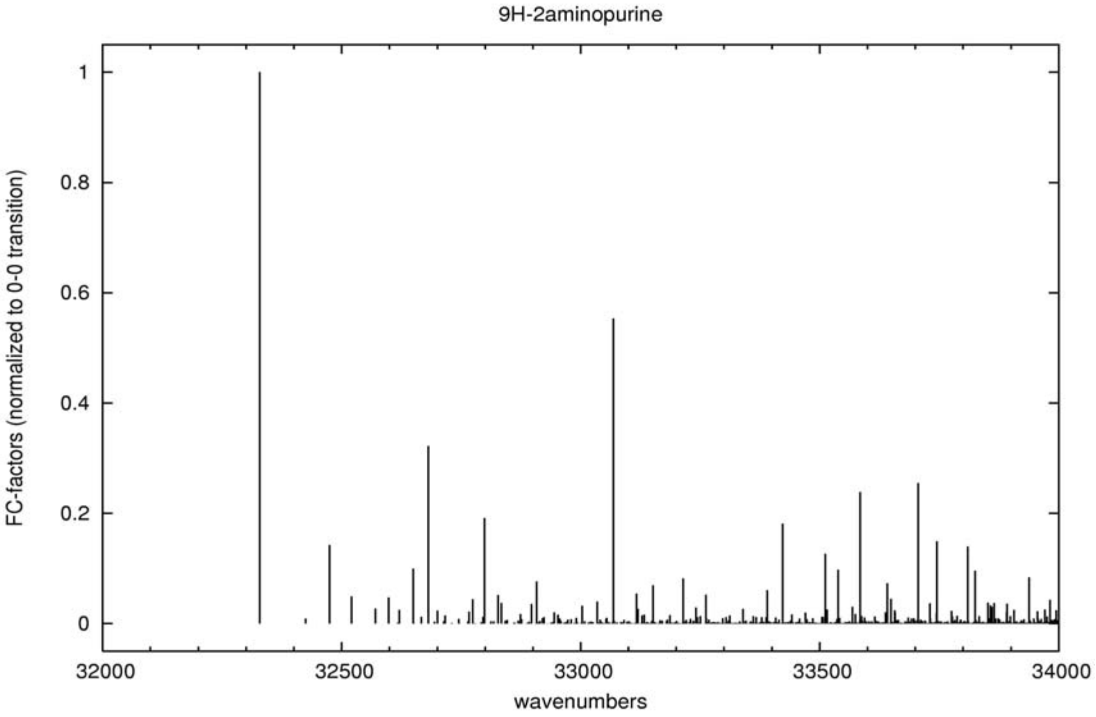
Table S1. Geometry parameters [Å] obtained from (TD)DFT calculations on electronic ground and excited states of 9H-2AP and 7H-2AP employing the B3LYP functional.

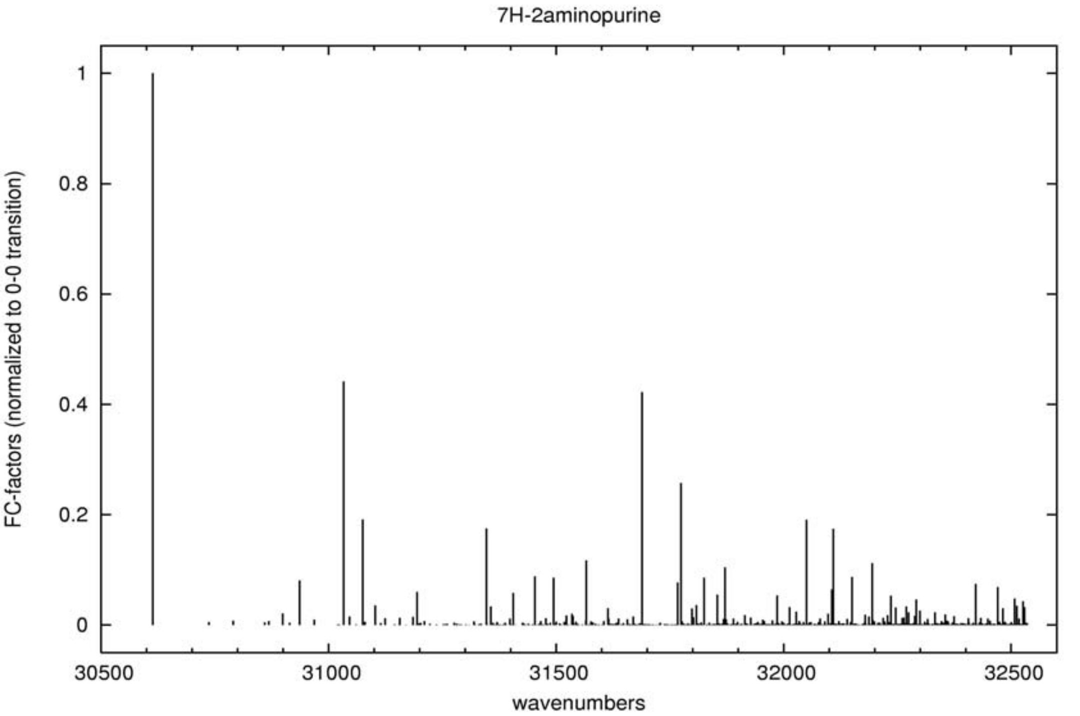
	9H-2aminopurine			7H-2aminopurine		
Bond	GS	$^1\pi\pi^*$	$^1n\pi^*$	GS	$^1\pi\pi^*$	$^1n\pi^*$
N_1-C_2	1.354	1.325	1.298	1.357	1.327	1.315
C_2-N_3	1.342	1.365	1.363	1.337	1.342	1.332
N_3-C_4	1.324	1.342	1.347	1.330	1.358	1.366
C_4-C_5	1.407	1.416	1.409	1.412	1.432	1.418
C_5-C_6	1.390	1.426	1.425	1.384	1.397	1.391
C_6-N_1	1.329	1.377	1.363	1.327	1.380	1.376
C_4-N_7	1.388	1.358	1.353	1.385	1.362	1.376
N_7-C_8	1.300	1.337	1.318	1.369	1.411	1.387
C_8-N_9	1.387	1.361	1.391	1.308	1.317	1.331
N_9-C_4	1.372	1.379	1.358	1.380	1.355	1.340
C_2-N_{10}	1.365	1.370	1.372	1.368	1.385	1.366

Figure Captions

S1. Computed vibronic $^1\pi\pi^*$ spectrum of 9H-2AP (upper panel) and 7H-2AP (lower panel). The intensities have been normalized to the strongest peak, i.e., the 0-0 transition.

Fig. S1


9H-2aminopurine
FC-factors (normalized to 0-0 transition)
1
0.8
0.6
0.4
0.2
0
32000
32500
33000
33500
34000
wavenumbers


7H-2aminopurine
FC-factors (normalized to 0-0 transition)
1
0.8
0.6
0.4
0.2
0
30500
31000
31500
32000
32500
wavenumbers